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Yucca Mountain Site Characterization Program

Milestone Report 3350

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Glossary of Acronyms

DOE	United States Department of Energy
e	extinction coefficient in $M^{-1}cm^{-1}$
EXAFS	Extended X-ray absorption fine structure
I	ionic strength
J-13	refers to a particular well drilled in the vicinity of Yucca Mountain
M	molarity (moles/liter)
NMR	Nuclear Magnetic Resonance Spectroscopy
PAS	Photoacoustic Absorption Spectroscopy
PZT	Lead Zirconate Titanate Piezoelectric Transducer
UE-25p #1	refers to a particular well drilled into the underlying (paleozoic) aquifer under the Yucca Mountain region
YMP	Yucca Mountain Site Characterization Program
z_i	charge of species labelled “i”

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ABSTRACT

The stability fields for dilute Pu-carbonate species versus pH (8.4 to 12.0) and total carbonate concentrations (3 mM to 1.0 M) have been mapped-out using photoacoustic absorption spectroscopy (PAS). At least four different plutonium species, characterized by absorption peaks at 486, 492, 500, and 513 nm, have been found. A redox change to a Pu(VI) complex can not account for the speciation change associated with the first two spectra (486 and 492 nm peaks). Moreover, the data are consistent with what is predicted from a previous YMP milestone (Hobart, Palmer, and Newton, 1986). This previous study was performed under very different conditions of plutonium concentration and carbonate/pH changes, and extension of these conditions to much lower Pu concentrations and to more neutral pHs was made possible with PAS spectroscopy. These new results reinforce the previous results by extending the range of direct observation and by eliminating other possibilities such as dimerization/polymerization reactions. As bicarbonate concentration is increased from .01 M to 1.0 M at pH=8.4 to 8.9, predominately $[Pu(OH)_{x+1}(CO_3)_y]^{4-(x+2y)}$ (492 nm peak) is converted to $[Pu(OH)_x(CO_3)_{y+1}]^{4-(x+2y+2)}$ (486 nm peak). The starting stoichiometry (x and y values) remain undetermined, but the effect of ionic strength and temperature indicate that the 486 nm species is highly charged, and therefore $x+2y \geq 3$. The temperature effect on the equilibrium between these two species was also investigated, with the species giving rise to the 486 nm peak reversibly losing importance at elevated (50 and 75°C temperatures.

INTRODUCTION

To understand the possible migration/retention of nuclear wastes from a potential long-term repository in the worst-case event of water infiltration, solubility and sorption studies of transuranic elements such as plutonium must be undertaken.[1,2] Ultimately, bulk solubility and sorption characteristics derive from molecular-level considerations of actinide speciation, which include inner-sphere coordination and nucleation (i.e. possible polymeric species) as well as valence state. Speciation studies have had a longstanding history in inorganic chemistry for a wide variety of solution complexes such as transition metal cations, and extension to the transuranics is a natural progression from classical inorganic chemistry.

To be relevant for radionuclide repository issues, a realistic choice of actinide and potential ligand must be made. Plutonium is a significant product in spent nuclear fuel, and from considerations of standard oxidation potentials and hydrolysis reactions, plutonium(IV) could be an important valence state under pH and E_h conditions expected for natural groundwaters.[3] As relevant potential ligands, carbonates are expected to be readily available, either as leachates from cement enclosures of a radioactive waste repository or from natural groundwaters.[3-5] Site-specific guidelines come from wells nears Yucca Mountain, Nevada, which is presently the only potential candidate being characterized for long term burial of high level nuclear waste in the United States. The total carbonate concentration, mostly as bicarbonate, of J-13 water taken from Yucca Mountain wells has been measured at 118 - 143 mg/liter $\simeq$ 2.8 mM[3], while paleozoic water from the deeper UE-25p#1 well tapping a carbonaceous aquifer under Yucca Mountain contains five times more carbonate.[3] Therefore, detailed knowledge of Pu(IV)-carbonate speciation is needed to predict migration/retention characteristics of plutonium.

To that end, speciation-sensitive absorption bands in the electronic spectra of actinides can be used to monitor actinide changes with environment.[6] Actinide visible absorptions are dominated by f-f transitions,[6] and although f-electrons are largely shielded from covalent interactions and hence produce very sharp spectra, the spectra do shift with electrostatic changes induced by changes in speciation. However, for these weak parity-forbidden f-f bands to be observed under conditions approaching environmental relevance (near neutral pH, radionuclide concentrations in the tens of nanomolar range), sensitive techniques such as pulsed photoacoustic absorption spectroscopy (PAS)[7] must be employed. Low concentrations are crucial to Pu(IV) speciation determinations because they minimize polymerization and the redox-altering reactions of radiolysis and Pu(V) disproportionation. In this milestone, we report our results from such PAS experiments on dilute Pu carbonate. While the structures of the Pu complexes giving rise to the absorption peaks cannot be determined solely on the basis of these data, this study does map-out predominance regions of interest and addresses important Pu nuclearity and oxidation state questions. Future studies from more structure-specific (but less sensitive) techniques such as NMR, EXAFS, and X-ray crystallography may subsequently allow us to match these optical absorbance signals with definite complexes.

EXPERIMENTAL

A stock of 1.4 mM ^{242}Pu(IV) in 3.00 M sodium carbonate solution served as our actinide source. The Pu stock was made by first dissolving (as Pu(III)) the pure metal in 6M HCl, followed by electrolytic oxidation at 1.2 V vs. NHE as described elsewhere.[8] Conventional UV/Vis spectroscopy (Perkin Elmer Lambda 9) was used to confirm sample integrity during the course of the experiments (2 years). A stock of ^{242}Pu(VI) in 1.0 M sodium carbonate solution was made by fuming a 1M $HClO_4$ solution of Pu(IV) almost to dryness and then adding carbonate. Again, conventional UV/Vis spectroscopy confirmed the identity of our Pu(VI) stock. The 242-isotope is 15.5 times less radioactive than ^{239}Pu and 4400 times less active than ^{238}Pu and allowed us to work outside of gloveboxes. Sodium carbonate (J.T. Baker, 'Baker Analyzed' reagent grade), sodium bicarbonate (Mallinckrodt, analytical reagent grade), and sodium perchlorate (EM Science, guaranteed reagent grade) were used as received. Solutions were filtered with 1 micron Acrodisc CR PTFE syringe filters, and the pH was measured with an ORION model 290-A meter and a ROSS combination electrode. Solutions were rapidly placed into cuvettes tightly stoppered with a Teflon stopper, and the spectra were typically taken within 15 hours, although some were taken up to 60 hours after solution preparation. Because the partial pressure of CO_2 was not rigorously controlled, small losses of carbonate could have occurred. Indeed, small pH changes were noted in the solutions after about a week, but these were negligible with the solutions used here.

The pulsed photoacoustic instrument used here has been described in detail elsewhere.[9] The third harmonic (355 nm) from a 10 Hz Nd/YAG Q-switched laser (Quanta-Ray DCR-3) was used to pump a dye laser (Quanta-Ray PDL-2) with coumarin 460, 480, or 500 laser dye (Exciton, Inc.). The 5 ns output pulse (at 6 mJ/pulse) was focused just beyond a stoppered 2.0 cm quartz cell containing the filtered plutonium sample. The spectral signal resulted from a shock wave produced by excited-state energy dissipation from an absorbing species, where the shock wave intensity is proportional to the absorbance at a particular wavelength. A spectrum was composed from multiple readings (typically 640 laser shots) at successive wavelengths. The shock wave was converted to an electrical signal by a shielded piezoelectric transducer (PZT) and amplified / filtered by two cascaded Stanford Research Systems SR560 amplifiers (x200 each). The signal was further filtered with two 10th order high pass, 1st order low pass passive filters described previously[9] (bandpass from 100 kHz to 1.3 MHz) and read by a digital oscilloscope (Hewlett-Packard 54111D). The wave was digitally rectified and the PAS signal integrated. The precision in the readings is represented by the ± 2 standard deviation of the mean (95% confidence level) error bars. The data presented are single-beam spectra. References (water + (bi)carbonate blank, measured under the same conditions and cells as the sample spectra) were subtracted from the Pu spectra. Elevated temperatures were achieved by placing the cuvette in a metal block through which thermostatted water (accurate to ± 1°C) was flowed. The heated cuvette was separated from the PZT by a quartz rod.

RESULTS AND DISCUSSION

The initial impetus for this work was a previous study[10] exploring speciation changes of Pu(IV) carbonates versus pH using optical spectroscopies. Specifically, this previous report claimed the existence of three species, $[Pu(CO_3)_5]^{6-}$, $[Pu(CO_3)_4]^{4-}$, and $[Pu(CO_3)_3]^{2-}$, in 1 M (bi)carbonate solutions between pH = 10.6 and pH = 8.8 based on their numeric fit to data at 425, 444, 474, and 486 nm. However, no new peaks were observed in the series used for the fit, and further analysis on the number of species present seemed warranted. A classic method to determine the number of species present in a series of spectra is to plot the extinction coefficients at various wavelengths versus that at another wavelength (usually the one with the largest change in e); a linear plot indicates only two species contribute significantly to the absorbances at the chosen wavelengths, while a non-linear plot indicates more than two contributing species.[11] From the data presented in ref. 10, a pH dependent plot of e(425), e(444), and e(474) vs. e(486) is linear, indicating only two species present (see Fig. 1).

Furthermore, as the pH was reduced further in this previous study (8.80 to 8.25), PAS measurements indicated that a new peak appeared at 492 nm at a total carbonate concentration of 1.0 M. Because of a precipitation reaction, the concentration of plutonium was different at each pH, varying from 120 mM at pH=8.80 to 1 mM at pH=8.25 (i.e. saturated solutions were used throughout). Therefore, a total of four species (4, 5, and 6 carbonate complexes of Pu and the species producing the 492 nm peak) were claimed,[10] although Fig. 1 presented here would argue for two species plus the 492 species (three in all).

To further test the number of species actually present as a function of pH, we systematically changed pH with constant [Pu] and constant total carbonate (i.e. constant $[CO_3^{2-}] + [HCO_3^-]$). This change was

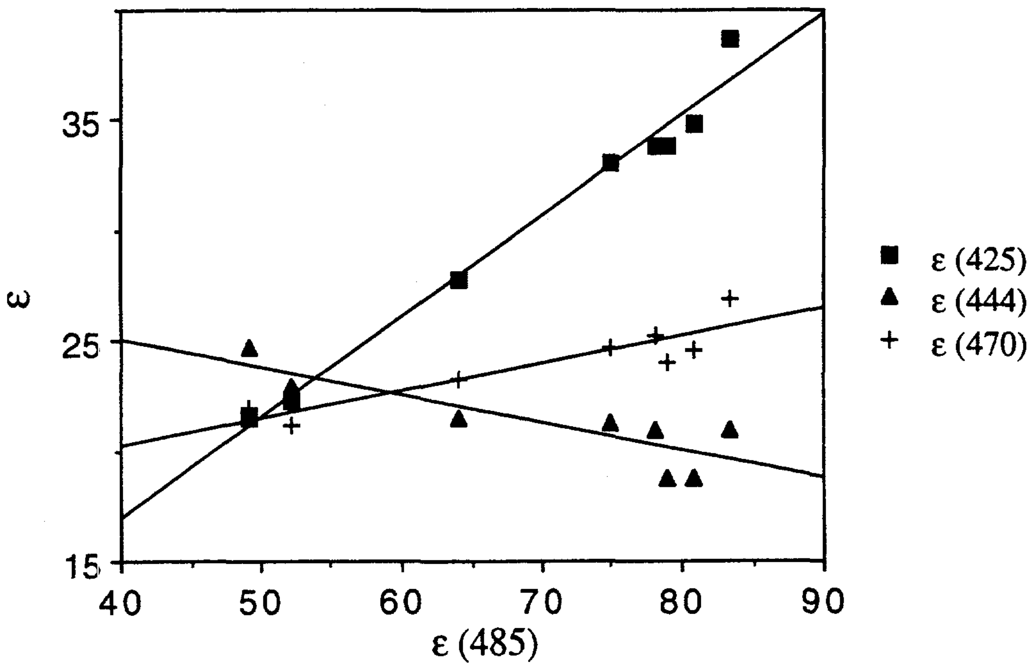

Fig. 1. Linear fits to data presented in reference 13 demonstrating that only two species are required to account for the absorption data.

accomplished by making a Pu-bicarbonate "stock" solution and moving to higher pH's with the addition of microliter amounts of a concentrated NaOH solution. With this general trend to higher pH's, no large amounts of acids were added[12] that would tend to quickly decrease the (bi)carbonate concentration through formation and loss of CO_2. A maximum concentration of 1 mM Pu(IV) was chosen because it was the lowest concentration used in the previous study[10] and therefore avoided the possibility of precipitation. The results of these experiments, as summarized in Figs. 2 and 3, show that only the 486 nm peak is observed in the 475 to 499 nm spectral region from pH 8.37 (Fig. 2) to 14 (Fig. 3). The lack of a distinct 492 nm peak in any of the spectra is in marked contrast to the previous reports discussed above[10,13] but is consistent with an isolated spectrum reported for a concentrated plutonium solution ([Pu] = 0.6 M in 1.0 M $NaHCO_3$).[14]

To pursue this unexpected result and to try to reconcile the studies, we varied the concentration of total (bi)carbonate at distinct pH's. At high pH (pH = 11.3), the 486 nm peak is replaced with one at 500 nm as the carbonate concentration is changed from 1.0 to 0.1 M (Fig. 4; a and b). However, because such high pH's are unlikely in a repository or natural environment, we have focused on pH's in the more neutral 8.5 range. In this restricted pH range, the solution $[HCO_3^-]/[CO_3^{2-}]$ ratio is at least 50 (at pH=8.6 with a pK_a of 10.3) and is therefore predominately bicarbonate throughout the range. The previously reported[10] 492 nm peak is now observed (Fig. 5), arising from a change in total (bi)carbonate concentration and not merely pH. A third species, associated with 3 and 12 mM bicarbonate concentrations at low ionic strength (determined by bicarbonate concentration only) and at 3 mM bicarbonate concentration at I=1.0 (with

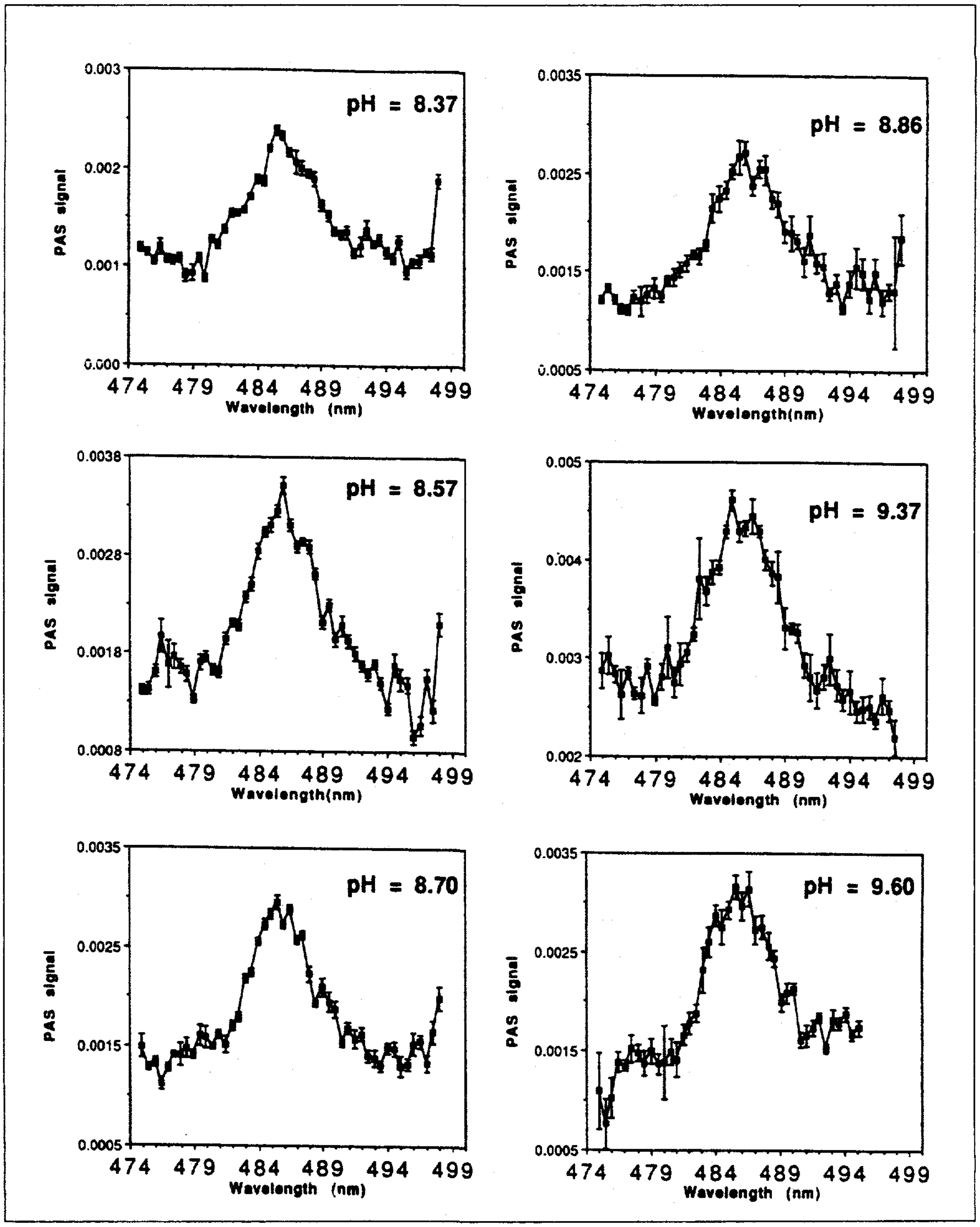

Fig. 2. Photoacoustic absorption spectra (PAS) of 1 mM Pu(IV) and 1.0 M total carbonate as a function of pH. Only the 486 nm peak is found, and it persists throughout the entire pH region. For an idea of the optical densities involved, note that the extinction coefficient of this peak has been measured previously to be 90 $cm^{-1}M^{-1}$,[3] so the absorbance at 486 nm in Fig. 2 would be 0.00018.

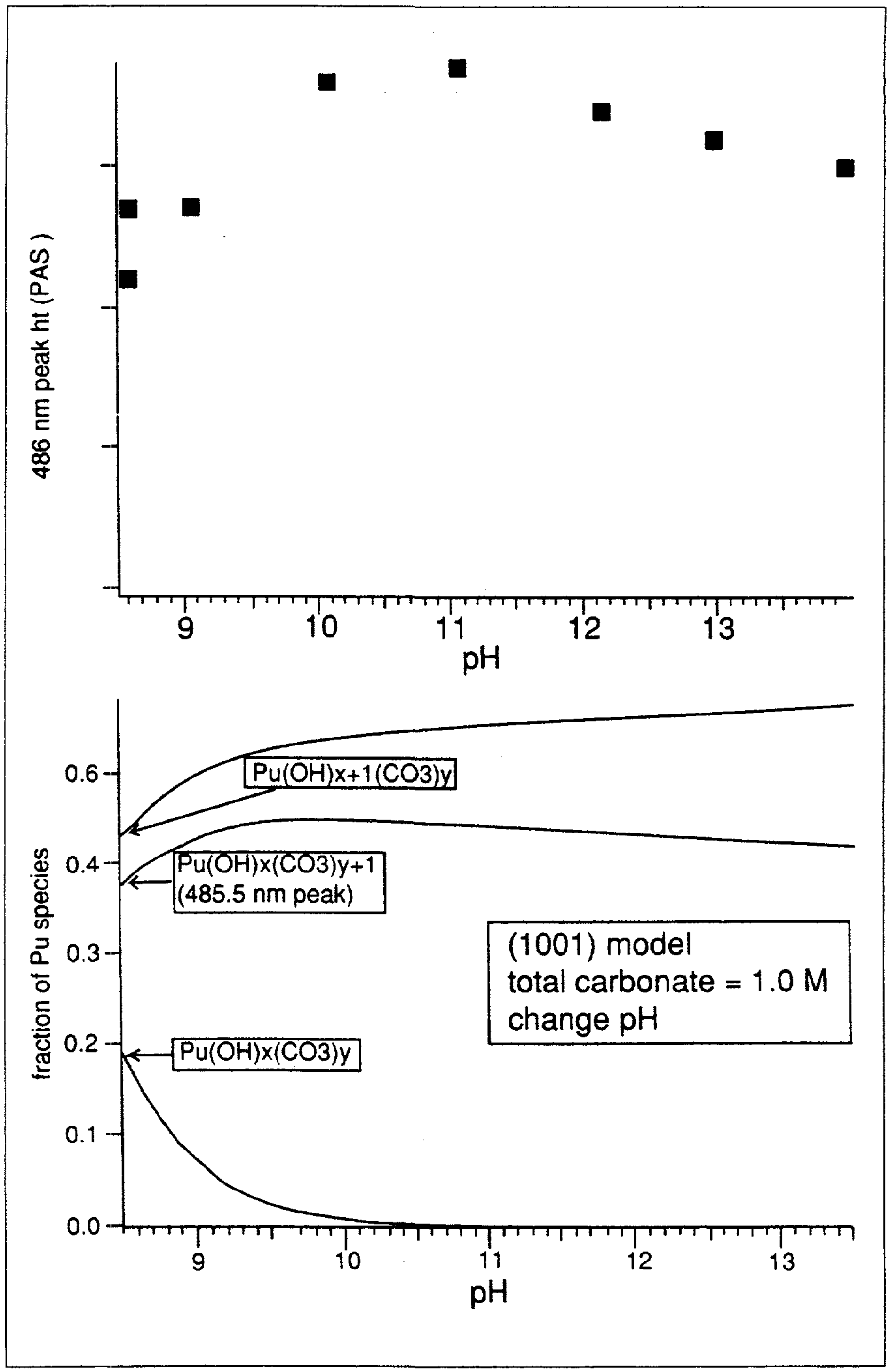

Fig. 3. a. Peak heights (arbitrary PAS units) of the 486 nm peak from a solution of 500 nM Pu(IV) and 1.0 M total carbonate as a function of pH over a broader range of pH than covered in Fig. 2.

b. Predicted speciation of plutonium complexes using the competitive model reactions discussed in reference 16.

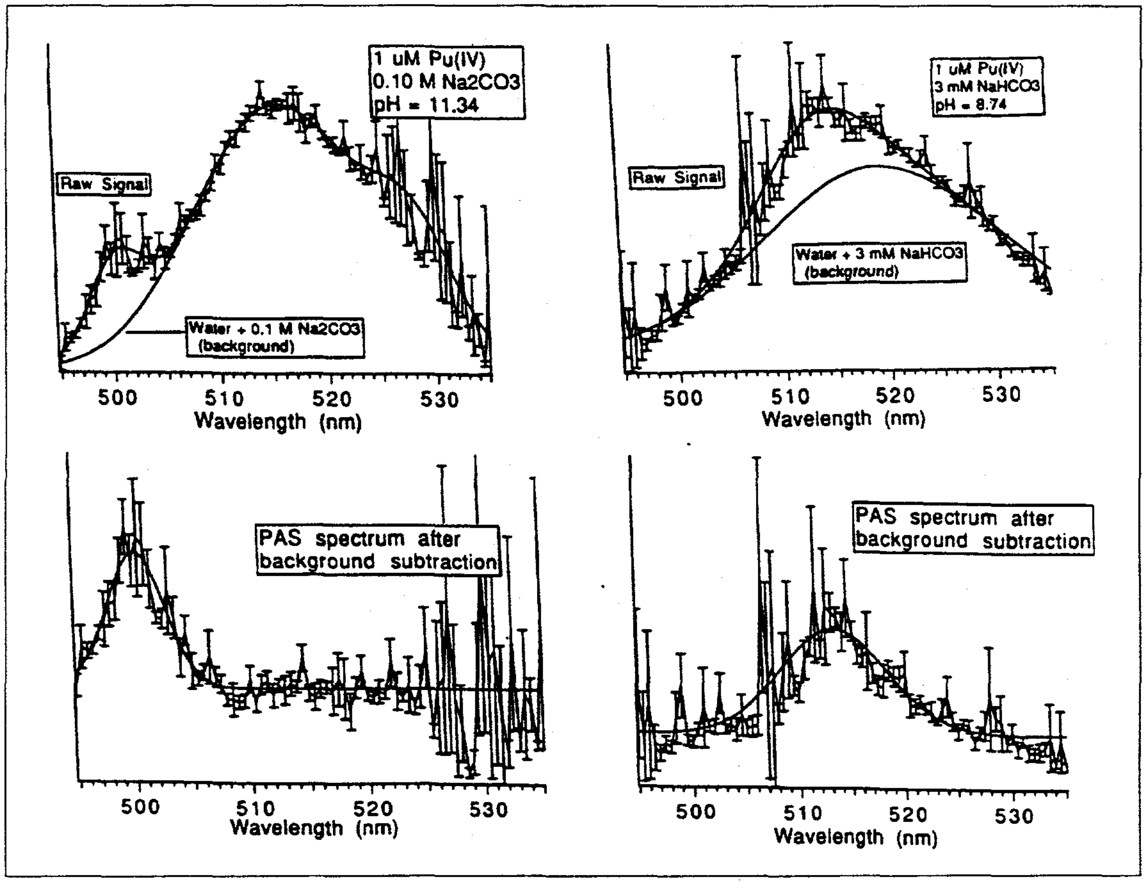

Fig. 4. PAS of 1 mM Pu in 0.10 M Na_2CO_3 (a and b) and in 3 mM $NaHCO_3$ (c and d). Spectra a and c are raw single-channel spectra which include water/carbonate backgrounds as well as the plutonium signal. Spectra b and d represent background-subtracted spectra. The parameters for the background fit were set from separate experiments with only water and (bi)carbonate (no Pu) present.

sodium perchlorate supporting electrolyte), was marked by a feature at 513 nm (Fig. 4b). Generally, then, a blue shift (513 --> 492 --> 486 nm) is exhibited with increasing bicarbonate concentration.

Fig. 5 shows the effect of changing the bicarbonate concentration from 1.0 to 0.01 M with constant ionic strength of 1.0 (with $NaClO_4$ as supporting electrolyte). A similar series of spectra with even lower plutonium concentration (250 nM) show that precipitation is not occurring in these spectral series, as the solubility of Pu in J-13 water (2.8 mM total carbonate) at pH=8.5 has been reported[15] to be 290 nM. A point to notice from Fig. 5 is that the 492 nm peak may always be present but becomes hidden by the strong 486 nm peak that appears at $[HCO_3^- + CO_3^{2-}] \geq 200$ mM.

These plutonium speciation changes occur over a small range of bicarbonate concentration. Figure 6a shows the result of an extensive series of PAS experiments in which the 486 nm absorption strength (vs. the constant absorption strength at 498 nm (see Fig. 5) and normalized for comparison) vs. bicarbonate concentration is plotted for several plutonium concentrations. If a change in nuclearity were occurring

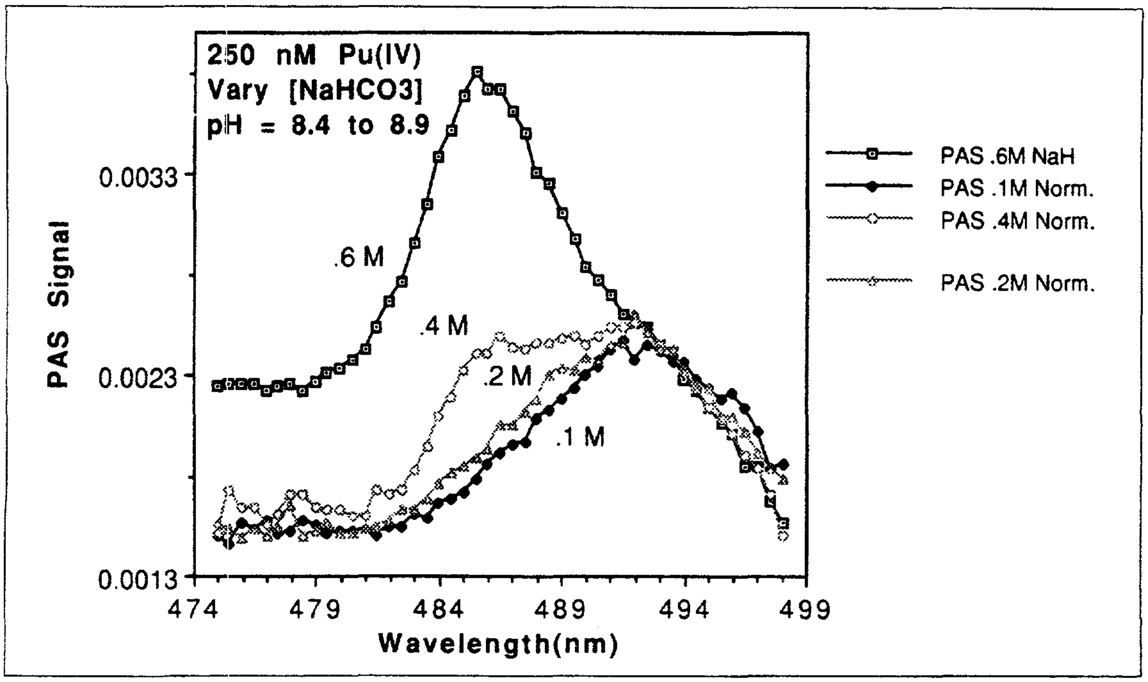

Fig. 5. PAS of 250 nM Pu at pH between 8.4 and 8.9 as a function of bicarbonate concentration with a constant total ionic strength of 1.0 M.

during this transition, the curves would be offset along the bicarbonate axis. However, the lack of offset in Fig. 6a demonstrates that the Pu nuclearity does not change, and the low plutonium concentrations studied by the PAS technique (down to 100 nM) suggests that these are monomeric species. A previous study[16] using concentrated plutonium concentrations and varying (bi)carbonate concentration (by equilibrating solutions with fixed CO_2 partial pressures) and pH simultaneously (to keep the Pu in solution) tentatively identified the following simultaneous reactions as the best fit to their data (absorbances at 668, 491, 485, and 424 nm):

$$Pu(OH)_x(CO_3)_y^{4-(x+2y)} + CO_2 + H_2O \Longleftrightarrow Pu(OH)_x(CO_3)_{y+1}^{4-(x+2(y+1)} + 2H^+$$

486 nm

and

$$Pu(OH)_x(CO_3)_y^{4-(x+2y)} + H_2O \Longleftrightarrow Pu(OH)_{x+1}(CO_3)_y^{4-(x+1+2(y)} + H^+$$

492 nm

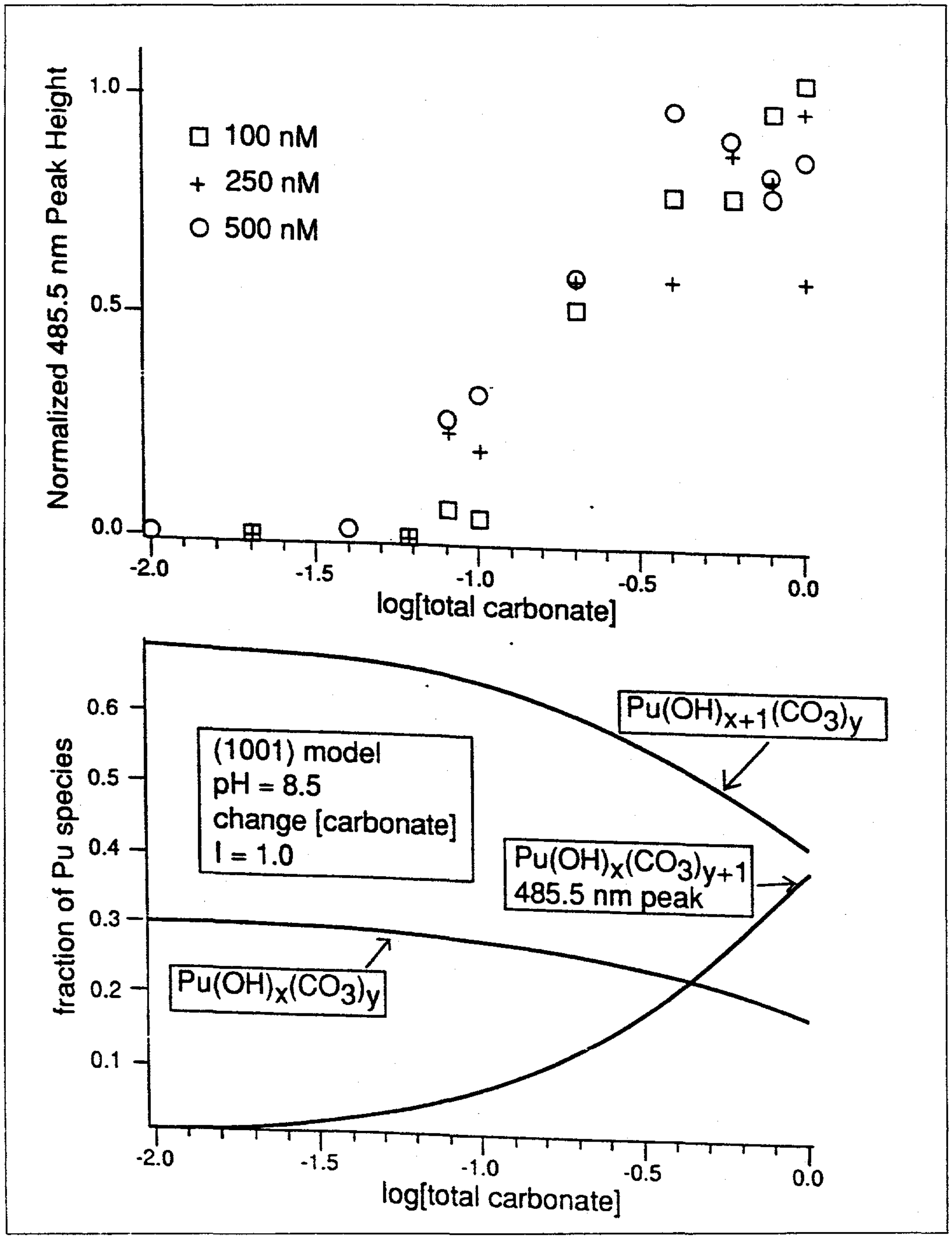

Fig. 6. a. Normalized absorbance of the 486 nm peak plotted vs. total carbonate concentration at pH=8.5. The plutonium concentrations used are 100, 250 and 500 nM.

b. Predicted species distribution for the three plutonium species vs. [bicarbonate].

The corresponding pQ's (i.e., -log(equilibrium constant)) for the two reactions are 15.72 and 8.14 respectively. The formulation of the base Pu species, $Pu(OH)_x(CO_3)_y{}^{4-(x+2y)}$, is meant to represent a general form due to our present lack of specific knowledge and assuming only that the species is monomeric. Figure 6b shows the species' mole fraction distribution calculated from these pQ's along the experimental route taken in Figs. 5 and 6a (i.e., constant pH, varying [bicarbonate]), and the agreement with our experimental results (Fig. 6a) is noted. The assumption of monomeric species is therefore further justified.

The large change in $\Sigma\Delta z_i^2$ on each side of chemical equations is also consistent with the spectral behavior at lower ionic strengths. The curve of the 492 <--> 486 nm transition is found to shift up 0.3 M HCO_3^- units at lower ionic strengths (i.e. when the ionic strength is not held constant but is instead set by bicarbonate concentration only). Because of the salting-in effect, then, z^2 for the 486 nm species must be considerably larger than that for the 492 nm species. In fact, this increased z^2 for the 486 nm species, together with the effect of coordinating negative ligands to Pu(IV) and that the last step is the addition of CO_3^{2-}, imply that the charge for the 486 nm species must be less than or equal to -1. Hence, $4-(x+2(y+1))\leq-1$, or $x+2y\geq3$.

Redox reactions must also be considered in any speciation study. The absorption spectrum for a radionuclide is diagnostic of its oxidation state,[17] and the weaker absorbances for the 492 nm species may be caused by a valence state change resulting in stronger peaks in different spectral regions. Indeed, previous solubility studies[15,18,19] with J-13 water (2.8 mM HCO_3^-) and UE-25p#1 water (11.4 mM HCO_3^-) at pH=8.5 concluded that the percentages of Pu(IV):Pu(V):Pu(VI) were 6:63:27 in J-13 and 31:64:2 in UE-25p#1 waters. However, this determination was indirect and involved potentially oxidation-state-altering acidification and partitioning (into coordinating organic ligands) steps.[20] Moreover, the difference between the oxidation state distribution for these two samples seems large given the speciation diagram presented here. Specifically, only one species, characterized by a 513 nm peak over the wavelength range 455 to 535 nm, was found for both 3 and 12 mM $NaHCO_3$ solutions at low ionic strength, hence implying that the 3 and 11 mM $NaHCO_3$ samples studied in the solubility study should be predominately the same Pu species. We therefore hoped to use absorption spectroscopy to probe the oxidation states. Unfortunately, the $[Pu(V)O_2]^+$ moiety absorbs only weakly in the visible region, peaking between 550 and 600 nm where Pu(IV) also has a comparable absorbance.[17] However, the $[Pu(VI)O_2]^{2+}$ moiety absorbs strongly below 500 nm in carbonate solutions,[14,17] unlike Pu(IV) and Pu(V) species, and we could look for a strong absorption tail at wavelengths less than 500 nm as a diagnostic for the presence of Pu(VI).

Figure 7 shows the spectra for freshly prepared Pu(IV) and Pu(VI) control solutions in 1M (bi)carbonate and the pH=8.7 "test" Pu solutions at 0.1 M bicarbonate (representing the species with the 492 nm absorbance signature) and 0.003 M bicarbonate concentration (representing the complex in J-13 and UE-25p#1 waters with the 513 nm absorbance signature). The strong absorbance at 486 nm (c.f., Fig.1) is diagnostic of a Pu(IV) species and allows us to use this solution as the Pu(IV) paradigm in agreement with other workers.[17] Furthermore, previous NMR experiments with the Pu(VI) carbonate indicated that the oxidation state of this solution does not change, at least over the course of several weeks[21] and therefore this solution could be used as our Pu(VI) paradigm. While the absorbance of the Pu(IV) solution increased by only 0.05 units from 480 to 450 nm, the Pu(VI) solution increased by 0.20 units. Therefore, this control experiment shows that we can indeed identify the presence of the 6+ oxidation state in an unknown solution.

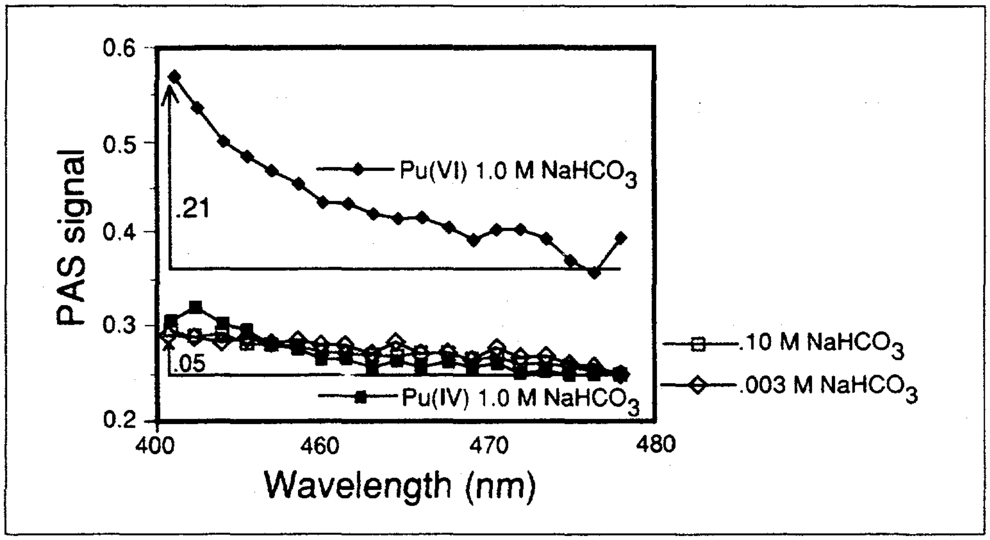

Fig. 7. Plutonium oxidation state determination using the characteristic blue/violet absorption of Pu(VI). This absorbance is shown by the freshly prepared Pu(VI) / 1.0 M Na_2CO_3 sample relative to the freshly prepared Pu(IV) / 1.0 M $NaHCO_3$, where neither of these species is expected to show a fast redox change. The two unknown species with lower bicarbonate concentrations are seen to lack this Pu(VI) absorption and is consistent with a Pu oxidation state of 4+ or 5+ (or a combination of both). The Pu concentration for all samples is 250 nM.

The two 250 nM Pu solutions of unknown oxidation state were made in 0.10 and 0.003 M $NaHCO_3$. The absorbance of both solutions increased only 0.05 units from 480 to 450 nm, essentially the same as the Pu(IV) species and substantially less than the Pu(VI) complex. Therefore, Pu in the 6+ oxidation state is essentially absent from these solutions, thereby disagreeing with the previous result from J-13 water[15,18] which reported 27% Pu(VI). Note that our sample was measured without chemical intervention. However, our sample had equilibrated for only about 1 day and not for 6+ months as in the solubility experiment. Furthermore, we have not discriminated between Pu(IV) and Pu(V), and although Pu(V) disproportionates to Pu(IV) and the readily detectable Pu(VI) in more concentrated Pu solutions, the low concentrations used here may minimize this reaction. These results, then, are not necessarily in disagreement with ref. 19, which reports essentially all Pu as Pu(V). To test this reference further, we note that at 60°C, 86% of the Pu was reported to be in the form of Pu(VI).[19] We are currently pursuing these experiments at elevated temperatures.

Finally, we investigated the temperature dependence of the Pu-carbonate speciation at 0.4 M total carbonate and ionic strength = 0.4 M , where speciation vs. [bicarbonate] is changing rapidly (see Fig. 5). Elevated temperatures are expected near any radionuclide repository due to the heating from released fission energy. Because the coefficient of expansion for water is larger at higher temperatures, the PAS signal should almost double over the temperature range from 20 to 90°C.[7] The spectra in Figure 8 have not been corrected for this effect, and only relative changes should be noted. The 492 nm peak reversibly gains intensity relative to the 486 nm peak at higher temperatures. An important solution change that would result in a reversible speciation change is a decrease in the dielectric constant of water at elevated

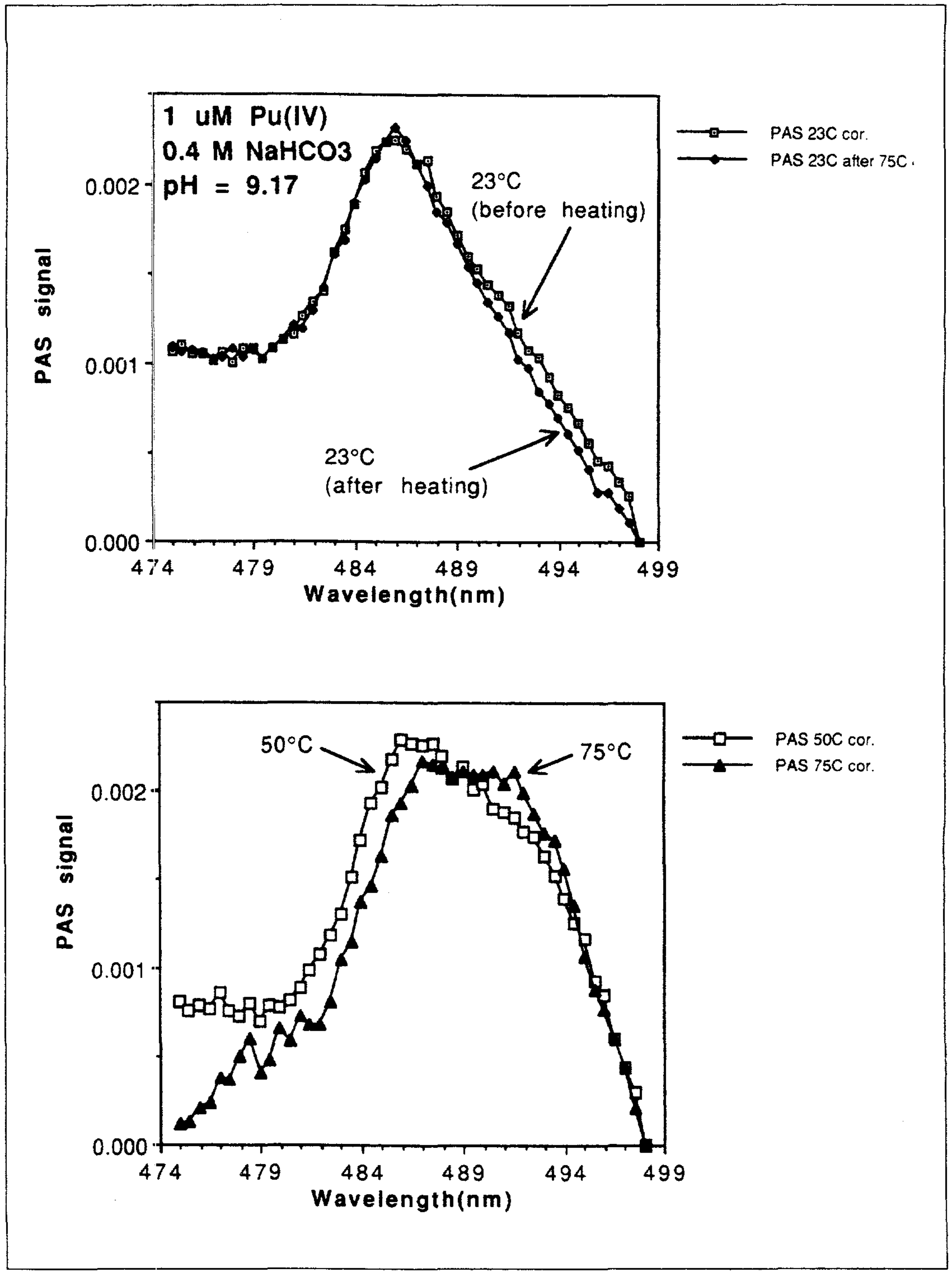

Fig. 8. Temperature dependence for 1.0 mM Pu at 0.4 M $NaHCO_3$ and pH = 9.17. The relative intensity of the 486 nm peak diminishes with respect to the 492 nm peak at higher temperatures, indicating a change in the equilibrium constant between the species contributing to the spectra. This change is reversible: the same spectrum is found at 23°C before and after the temperature increase.

temperatures.[22] This lowered dielectric constant will destabilize a more highly charged species relative to one with a lower charge, consistent with overall carbonate loss from a highly coordinated complex and consistent with the model proposed above. Besides this physical effect, a chemical effect to the standard enthalpy change of a reaction comes from bond formation / breaking. Collectively, the standard enthalpy change produces temperature changes in an equilibrium constant through the well known van't Hoff equation.

CONCLUSIONS

In contrast to a previous report,[10] a single plutonium(IV) species with a 486 nm absorption signature dominates in 1.0 M total carbonate solutions from pH 8.4 to at least pH 12. Other species with absorption peaks at 500 nm (0.1 M carbonate, pH=11), 492 nm (.4 to .03 M bicarbonate at low ionic strength and 0.01 M to 0.1 M at I=1.0M, pH=8.4 to 8.6), and 513 nm (12 and 3 mM bicarbonate, ionic strength set by bicarbonate, pH=8.8) have been identified. The species giving rise to the 486 nm peak is likely to be a highly charged monomer consistent with a high carbonate ligation field, as judged from its salting-in behavior and its reversible behavior at elevated temperatures. The red-shifted spectra are associated with species with lower carbonate coordination to the Pu center. The exact nature of these species is under investigation now at higher concentrations and using complementary techniques such as NMR and EXAFS. However, we can say that no oxidation state change to Pu(VI) has occurred, although a change to Pu(V) can not be ruled out. The use of PAS spectroscopy was necessary to extend Pu studies to as low a concentration as possible to help determine the nuclearity of the Pu(IV) reactions and the redox state of key solutions (by minimizing side reactions of Pu(V) disproportionation and radiolysis effects).

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REFERENCES

1. a. Nuclear Waste Policy Act (Section 113) "Site Characterization Plan, Yucca Mountain Site, Nevada Research and Development Area, Nevada". U.S. Department of Energy DOE/RW-199, Office of Civilian Radioactive Waste Management, Washington, D.C. 1988. (HQO.881201.0002)

   b. Code of Federal Regulations "General Guidelines for the Recommendation of Sites for Nuclear Waste Repositories." U.S. Department of Energy Title 10, Part 960, Washington, D.C. 1988. (NNA.910809.0013)

2. Brooks, D.J.; Corrado, J.A. in "Determination of Radionuclide Solubility in Groundwater for Assesment of High-Level Waste Isolation," U.S. Nuclear Regulatory Commission, Technical Position, Washington, D.C. 1984. (HQS.880517.2024)

3. Hobart, D.E. "Actinides in the environment" in *Proceedings of the Robert A. Welch Conference on Chemical Research XXXIV. Fifty Years with Transuranium Elements;* Ch. XIII, Oct. 22-23, 1990. (NNA.930405.0083)

4. Stumm, W. and Morgan, J.J. in "Aquatic Chemistry". John Wiley and Sons, New York 1981. (book, readily available)

5. Lindsay, W.L. in "Chemical Equilibria in Soils". John Wiley and Sons, New York, 1979. (NNA.900214.0215)

6. "The Chemistry of the Actinide Elements" (2nd ed., Volume 2), eds. J.J. Katz, G.T. Seaborg, L.R. Morss, Chapman and Hall, London. (book, readily available)

7. Tam, A.C. "Applications of photoacoustic sensing techniques" *Rev. Mod. Phys.* **1986**, *58*, 381-431. (NNA.940124.0039)

8. Newton, T.W.; Hobart, D.E.; Palmer, P.D. "The preparation and stability of pure oxidation states of neptunium, plutonium, and americium" Los Alamos report LA-UR-86-967, **1986.** (NNA.930406.0025)

9. Berg, J.M.; Tait, C.D.; Morris, D.E.; Woodruff, W.H. "Actinide speciation by photothermal spectroscopies: instrumental development" *Mat. Res. Soc. Symp. Proc.* **1991**, *212*, 531-538. (NNA.940124.0042)

10. Eisworth, M.; Kim, J.I.; Lierse, C. "Optical absorption spectra of Pu(IV) in carbonate / bicarbonate media" *Radiochim. Acta* **1985**, *38*, 197-201. (HQS.880517.3074)

11. Connors, K.A. in "Binding Constants: The Measuremet of Molecular Complex Stability", Wiley-Interscience (New York), 1987, 411 Pp. (book, readily available)

12. Small amounts of $HClO_4$ were occassionally added to fine-tune the pH, especially to get the most neutral pH used in the trials. However, our conservative approach of generally increasing pH instead of decreasing it as in ref. 13 may have resulted in their losing more carbonate concentration than anticipated and to the subsequent discrepancy between our experimental data and theirs.

13. Kim, J.I.; Lierse, C.; Baumgartner, F. in "Plutonium Chemistry". ACS Symp. Series **216**, 1983. (book, readily available)

14. Wester, D.W. and Sullivan, J.C. "The absorption spectra of Pu(VI), (V), and (IV) produced electrochemically in carbonate-bicarbonate media" *Radiochem. Radioanal. Letters* **1983**, *57*, 35-42. (NNA.931214.0044)

15. Nitsche, H.; Muller, A.; Standifer, E.M.; Deinhammer, R.S.; Becraft, K.; Prussin, T.; Gatti, R.C., "Depeendence of actinide solubility and speciation on carbonate concentration and ionic strength in groundwater" *Radiochimica Acta.* **1992**, *58/59*, 27-32. (NNA.940124.0043)

16. Hobart, D.E.; Palmer, P.D.; and Newton, T.W. "The carbonate complexation of Pu(IV)" Nevada Nuclear Waste Storage Investigations Interim Report LA-UR-86-968, 1986. (NNA.940217.0002) The identity of the original plutonium species, given by the general formula $Pu(OH)_x(CO3)_y{}^{4-(x+2y)}$, is not known. At pH=8.5 under bicarbonate conditions used, an approximate relationship between PCO_2 (atm) and [bicarbonate] is

$$PCO_2 = 0.000443 + 0.097618\,[\text{bicarb}] + 0.034081\,[\text{bicarb}]^2$$

17. Weigel, F.; Katz, J.J.; Seaborg, G.T. in *The Chemistry of the Actinide Elements,* Eds. J.J. Katz, G.T. Seaborg, and L.R. Morss, 2nd ed. (1986) Chapman and Hall, 499-886. (book, readily available)

18. Nitsche, H.; Gatti, R.C.; Standifer, E.M.; Lee, S.C.; Muller, A.; Prussin, T.; Deinhammer, R.S.; Maurer, H.; Becraft, K.; Leung, S. ; Carpenter, S.A. in "Measured Solubilities and Speciation of Neptunium, Plutonium, and Americium in a Typical Groundwater (J-13) from the Yucca Mountain Region" Milestone Report M-3010, Yucca Mountain Site characterization Project, U.S. Civilian Radioactive Waste Management Program, 1992. (Pre-assigned #: NNA.930507.0136)

19. Nitsche, H.; Roberts, K.; Prussin, T.; Muller, A.; Becraft, K.; Keeney, D.; Carpenter, S.A.; Gatti, R.C. in "Measured Solubilities and Speciations form Oversaturated Experiments of Neptunium, Plutonium, and Americium in UE25p#1 Well Water from the Yucca Mountain Site Characterization Program, 1992. Milestone 3329. (pre-assigned #: NNA.931015.0073)

20. Nitsche, H.; Lee, S.C.; Gatti, R.C. "Determination of plutonium oxidation states at trace levels pertinent to nuclear waste disposal" *J. Radioanal. and Nucl. Chem.* **1988**, *124*, 171-185. (NNA.930326.0099)

21. Clark, D.L.; Ekberg, S.A.; Morris, D.E.; Palmer, P.D.; Tait, C.D. "Actinide(IV) and Actinide Carbonate Speciation Studies by PAS and NMR Spectroscopies" Milestone Report 3031, Yucca Mountain Site characterization Project, U.S. Civilian Radioactive Waste Management Program, 1992. (NNA.931015.0074)

22. a. Brimhall, G.H.; Crerar, D.A. in "Thermodynamic Modelling of Geologic Materials: Minerals, Fluids, and Melts" (eds. I.S.E. Carmichael and H.P Eugster): *Reviews in Mineralogy* **17**, 255-321. (NNA.940323.0287)

    b. Seward, T.M. "The formation of lead(II) chloride complexes to 300°C; a spectrophotometric study" *Geochim. Cosmochim. Acta* **1984**, *48*, 121-134. (NNA.940124.0045)

Quality Assurance Documentation

Data in this paper are documented in laboratory notebooks TWS-INC-11-06-90-08, TWS-INC-11-06-91-06, TWS-INC-11-07-91-02, TWS-INC-07-92-13, TWS-INC-01-93-04, and TWS-INC-05-93-11. Some of the software used for data collection / manipulation has not been certified by the Yucca Mountain Site Characterization Program QA program. The Automated Technical Data Tracking Number for this report is pending.

Data Tracking Numbers: 000 000 000 076.001
000 000 000 076.002